

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 February 2006 (23.02.2006)

PCT

(10) International Publication Number
WO 2006/018403 A1

(51) International Patent Classification⁷: **C10M 129/00**,
129/72, 135/26, 141/06, 141/10, 141/08

(21) International Application Number:
PCT/EP2005/053883

(22) International Filing Date: 8 August 2005 (08.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/602,593 18 August 2004 (18.08.2004) US

(71) Applicant (for all designated States except US): **CIBA
SPECIALTY CHEMICALS HOLDING INC.** [CH/CH];
Klybeckstrasse 141, CH-4057 Basel (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **AL-AKH DAR**,
Walid [US/US]; 3407 Raleigh Way, Mobile, AL 36695
(US). **CHAFIN, Laura F.** [US/IT]; Via Gaudenzi
5, I-40137 Bologna (IT). **CHASAN, David Eliezer**
[US/US]; 1100 Windsor Road, Teaneck, NJ 07666 (US).

(74) Common Representative: **CIBA SPECIALTY CHEM-
ICALS HOLDING INC.**; Patent Department, Klybeck-
strasse 141, CH-4057 Basel (CH).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA,
MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ,
OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL,
SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC,
VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: LUBRICATING OIL COMPOSITIONS WITH IMPROVED PERFORMANCE

(57) Abstract: Disclosed are stabilized lubricating oil compositions with improved oxidative performance. These lubricating oil compositions contain certain phenolic antioxidants, in combination with other antioxidants, which contribute to the improved performance.

AL6

Lubricating Oil Compositions with Improved Performance

The present invention is aimed at lubricating oil compositions with improved oxidative performance.

WO 2000/22070 discloses a long life gas engine oil and additive system comprising a minor amount of phenolic antioxidants.

U.S. Patent Specification No. 5,711,767 discloses stabilizer systems for the prevention of gum formation in gasoline comprising phenolic antioxidants.

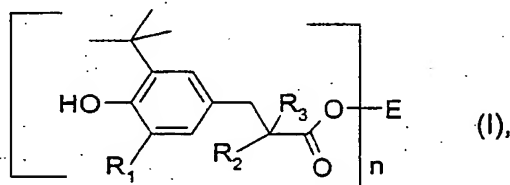
Titova, T. F. et al. in *Zhurnal Organicheskoi Khimii* **1984**, 20(9), 1899-905 disclose the synthesis of dimethyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate.

10 It has surprisingly been found that lubricating oil compositions containing certain antioxidants display improved oxidative performance.

The present invention relates to a lubricating oil composition with improved oxidative performance, said composition comprising

a) At least one hindered phenolic antioxidant compound of formula (I),

15



Wherein

R₁ is alkyl of 1 to 4 carbon atoms;

n is an integer from 1 to 4;

R₂ is H or has the meanings of R₃;

20

R₃ is $-(CH_2)_x-COOR_4$, where x is 1 to 10;

R₄ is straight or branched chain alkyl of 1 to 24 carbon atoms or the group of the partial formula E;

When n is 1, E is straight or branched chain alkyl of 1 to 24 carbon atoms;

25

When n is 2, E is straight or branched chain alkylene of 2 to 12 carbon atoms or said alkylene interrupted by one to five O or S atoms;

When n is 3, E is a straight or branched chain alkanetriyl of 3 to 6 carbon atoms; and

When n is 4, E is pentaerythrityl;

- b) At least one additional antioxidant compound; and
- c) A base fluid.

In the composition described above the percent by weight of component a) to the total weight of component a) plus component b) is about 0.001% to about 99.999%,

Alkyl is straight or branched chain and is for example methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, n-pentyl, isopentyl, n-hexyl, n-heptyl, 3-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, undecyl, n-dodecyl, tridecyl, n-tetradecyl, pentadecyl, n-hexadecyl, n-octadecyl, n-icosyl, heptadecyl, 2-ethylbutyl, 1-methylpentyl, 1,3-dimethylbutyl, 1,1,3,3-tetramethylbutyl, 1-methylhexyl, isoheptyl, 1-methylheptyl, 1,1,3-trimethylhexyl, and 1-methylundecyl.

Specific compounds of component a) include hindered phenolic antioxidant compounds of the formula (I) selected from the group consisting of:

Dimethyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate,

Diisooctyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate, and

Monomethyl-monoisooctyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate.

The antioxidant compounds of component b) in the compositions of the present invention are phenolic antioxidants.

Preferred phenolic antioxidants of component b) in the compositions of the present invention are selected from the group consisting of:

n-Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,

Isooctyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,

Neopentetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

1,3,5-tris(3,5-Di-tert-butyl-4-hydroxybenzyl)isocyanurate,

Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene,

3,6-Dioxaoctamethylene bis(3-methyl-5-tert-butyl-4-hydroxyhydrocinnamate),

2,6-Di-tert-butyl-p-cresol,

2,2'-Ethylidene-bis(4,6-di-tert-butylphenol),

- 1,3,5-tris(2,6-Dimethyl-4-tert-butyl-3-hydroxybenzyl)isocyanurate,
1,1,3-tris(2-Methyl-4-hydroxy-5-tert-butylphenyl)butane,
1,3,5-tris[2-(3,5-Di-tert-butyl-4-hydroxyhydrocinnamoyloxy)ethyl] isocyanurate,
3,5-Di-(3,5-di-tert-butyl-4-hydroxybenzyl)mesitol,
5 Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
1-(3,5-Di-tert-butyl-4-hydroxyanilino)-3,5-di(octylthio)-s-triazine,
N,N'-Hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide),
Calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate),
Ethylene bis[3,3-di(3-tert-butyl-4-hydroxyphenyl)butyrate],
10 Octyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate,
bis(3,5-Di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide,
N,N'-bis[2-(3,5-Di-tert-butyl-4-hydroxyhydrocinnamoyloxy)-ethyl]oxamide,
2,6-Di-tert-butylphenol,
2,4-Di-tert-butylphenol,
15 Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Pentaerythritol tris(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
Pentaerythritol di(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
tris(2,4-Di-tert-butylphenyl) phosphite,
Di-n-octadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate,
20 N,N-Di-(C₁₄-C₂₄alkyl)-N-methylamine oxide,
N,N-Dialkylhydroxylamine, and
N,N-Di(hydrogenated tallow)hydroxylamine.
- Particularly preferred phenolic antioxidants of component b) in the compositions of the present invention are selected from the group consisting of:
- 25 n-Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Isooctyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnammate),

Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

2,2'-Ethylidene-bis(4,6-di-tert-butylphenol),

1,1,3-tris(2-Methyl-4-hydroxy-5-tert-butylphenyl)butane,

Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

5 N,N'-Hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide),

Ethylene bis[3,3-di(3-tert-butyl-4-hydroxyphenyl)butyrate],

bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide,

2,6-Di-tert-butylphenol,

2,4-Di-tert-butylphenol,

10 Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,

Pentaerythritol tris(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

Pentaerythritol di(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), and

tris(2,4-Di-tert-butylphenyl) phosphite.

Highly preferred phenolic antioxidants of component b) in the compositions of the present in-

15 vention are selected from the group consisting of:

n-Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,

Isooctyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,

Neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

20 2,6-Di-tert-butylphenol,

2,4-Di-tert-butylphenol,

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,

Pentaerythritol tris(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

Pentaerythritol di(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), and

25 tris(2,4-Di-tert-butylphenyl) phosphite.

The base fluids in component c) in accordance with the invention utilize mineral oil based fluids (API Group I, II and III), lubricating oil base stock, poly-alpha-olefins – PAOs (API Group IV), esters (API Group V), other synthetic fluids, natural oils that are animal or vegeta-

ble in origin, and mixtures thereof. The base fluids are of suitable viscosity for utilization in engine oil applications.

The compositions are useful in lubricating oils. The present lubricating oils are for example those employed in internal combustion engines. The present oils have necessary lubricating viscosity. The oils are for example mineral oils or are synthetic and mixtures thereof.

The lubricating oil base stock can be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable lubricating oil base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude oil.

Natural lubricating oils include animal oils, vegetable oils (for example, rapeseed oils, castor oils, and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale.

Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils, such as polymerised and inter-polymerised olefins, alkyl benzenes, polyphenols, alkylated diphenyl ethers, alkylated diphenyl sulphides, as well as their derivatives, analogues and homologues thereof, and the like. Synthetic lubricating oils also include alkylene oxide polymers, inter-polymers, copolymers and derivatives thereof wherein the terminal hydroxy groups have been modified by esterification, etherification, etc. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids with a variety of alcohols. Esters useful as synthetic oils also include those made from C5 to C12 monocarboxylic acids and polyols and polyol ethers.

Silicon-based oils, such as the polyalkyl-, polyaryl, polyalkoxy, or polyaryloxy-siloxane oils and silicate oils, comprise another useful class of synthetic lubricating oils. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins, and the like.

The lubricating oil may be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (for example, coal, shale, or tar and bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydro treating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Rerefined oils are obtained by treating refined oils in proc-

esses similar to those used to obtain refined oils. These rerefined oils are also known as re-claimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

Lubricating oil base stocks derived from the hydroisomerization of wax may also be used,
5 either alone or in combination with the aforesaid natural and/or synthetic base stocks. Such wax isomerised oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over hydroisomerization catalyst.

Examples of natural waxes are the slack waxes recovered by the solvent dewaxing of min-
eral oils; synthetic waxes are the wax produced by the Fischer-Tropsch process. The result-
10 ing isomerised product is subjected to solvent dewaxing and fractionation to recover various fractions of specific viscosity indices, generally having a VI of at least 130, preferably at least 135 and higher and following dewaxing, a pour point of about -20°C and lower.

The production of wax isomerised oil meeting the requirements of the present invention is disclosed in *U.S. Patent Specification* Nos. 4,049,299 and 4,158,671.

15 Greases or other solid lubricants are also lubricating oils according to this invention.

The synthetic hydrocarbon oils include long chain alkanes, such as cetanes and olefin poly-
mers, such as trimer and tetramers of octane and decane. These synthetic oils can be mixed
with 1) ester oils, such as pentaerythritol esters of monocarboxylic acids having about 2 to 20
carbon atoms, 2) polyglycol ethers, 3) polyacetals and 4) siloxane fluids. Useful among the
20 synthetic esters are those made from polycarboxylic acids and monohydric alcohols. For ex-
ample, ester fluids made from pentaerythritol or mixtures thereof with di- and tripentaerythri-
tol, and an aliphatic monocarboxylic acid containing from 1 to 20 carbon atoms, or mixtures
of such acids. Other examples are ester fluids made from trimethylolpropane and an aliphatic
monocarboxylic acid containing from 1 to 20 carbon atoms, or mixtures of such acids.

25 The present lubricating oils are also for example crude oil, industrial lubrication oils, cutting
oil, metal working fluids and greases.

Fuels are also a base fluid according to the invention, for example certain aviation fuels and
the like, wherein lubrication properties are desired. The fuels are for example a hydrocarbo-
naceous petroleum distillate, such as motor gasoline, diesel fuel or fuel oil. Liquid fuel com-
30 positions comprising non-hydrocarbonaceous materials, such as alcohols, ethers, organo-ni-
tro compounds and the like (e.g. methanol, ethanol, diethyl ether, methyl ethyl ether, nitro-
methane) are also within the scope of this invention as are liquid fuels derived from vegeta-
ble or mineral sources, such as corn, alfalfa, shale and coal. Fuels that are mixtures of one
or more hydrocarbonaceous fuels and one or more non-hydrocarbonaceous materials are

also contemplated. Examples of such mixtures are combinations of gasoline and ethanol and of diesel fuel and ether.

The present additives provide extreme pressure, antiwear and friction reducing properties to the oil, and upon combustion, are innocuous to conventional catalytic converters in automobiles.

The percent by weight of component a) to the total weight of component a) plus component b) is for example from about 0.001 to about 99.999%. For instance the percent by weight of component a) to the total weight of a) plus b) is from about 0.05% to about 90.0%, from about 0.1% to about 50.0%, or from about 1.0% to about 10.0%.

The additive mixture of this invention, the combination of component a) and component b), are present in the oil composition in a total amount of for example about 0.01% to about 20.0% by weight of the total composition. For instance, the antioxidant compositions are present from about 0.05% to about 15.0%, from about 0.1% to about 10.0%, from about 0.2% to about 5.0% by weight, based on the weight of the entire composition. For example, the antioxidant compositions are present from about 0.1% to about 20.0%, from about 0.1% to about 15.0% or from about 0.1% to about 5.0% by weight, based on the weight of the entire composition.

In lubricating compositions operated under extremely adverse conditions, such as lubricating compositions for marine diesel engines, the additives of this invention may be present in amounts of up to about 30.0% by weight, or more, of the total weight of the lubricating composition.

The additives of this invention are present in the fuel compositions at a level of from about 1 ppm to about 50 000 ppm based on the fuel. For example the additives are present from about 4 ppm to about 5 000 ppm based on the fuel by weight.

Another object of the invention is the antioxidant mixture based on the combination of component a) and component b).

Thus, also disclosed are antioxidant compositions, which comprise a mixture of

a) At least one hindered phenolic antioxidant compound of formula (I), wherein R_1 , R_2 , R_3 , R_4 and E are as defined above; and

b) At least one additional antioxidant compound.

The present invention also relates to the above-defined composition additionally comprising

e) At least one organic material subject to the deleterious effects of oxidative, thermal, or light-induced degradation.

The invention furthermore relates to compositions comprising an organic material in component e) which is sensitive to oxidative, thermal, or light-induced degradation and at least one compounds listed in component a) formula (I) and at least one antioxidant compound listed in component b).

The invention also relates to a process for stabilizing an organic material in component e) which is sensitive to oxidative, thermal, or light-induced degradation, which comprises adding, to this material, at least one compound listed in component a) formula (I) and at least one antioxidant compound listed in component b).

Organic materials in component e), which would benefit from the incorporation of the antioxidants are polymers, for example synthetic polymers, in particular thermoplastic polymers. Particularly preferred organic materials in component e) are polyolefins and styrene copolymers, for example those mentioned in *U.S. Patent Specification No. 5,478,875* under items 1 to 3 and items 6 and 7. Especially preferred organic materials in component e) are for example polyethylene, polypropylene, ABS, and styrene/butadiene copolymers. The invention therefore preferably relates to compositions in which the organic material in component e) is a synthetic organic polymer or a mixture of such polymers, in particular a polyolefin or a styrene copolymer.

The invention also relates to a method of improving oxidative performance in a lubricating oil composition comprising

b) At least one antioxidant compound according to component b), as defined above; and

c) A base fluid,

which method comprises incorporating into said lubricating oil composition at least one compound of component a) formula (I) as defined above.

The lubricating oils stabilized in accordance with the invention may additionally or optionally include other additives, component d), which are added in order to improve still further the basic properties of these formulations; such additives include other antioxidants, metal passivators, rust inhibitors, corrosion inhibitors, viscosity index improvers, extreme pressure agents, pour point depressants, solid lubricants, dispersants, detergents, antifoams, colour stabilizers, further extreme pressure additives, demulsifiers, friction modifiers, and, antiwear additives. Such additives are added in the customary amounts in each case in the range

from in each case about 0.01% to 10.0% by weight, based on the lubricating oil. The text below gives examples of such additional additives:

Examples of antioxidants are:

- 1) Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-iso-butylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-(α -methyl-cyclohexyl)-4,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,4,6-tri-cyclo-hexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, linear or side chain-branched nonylphenols, for example 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methyl-undec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol or mixtures thereof;
- 2) Alkylthiomethylphenols, for example 2,4-di-octylthiomethyl-6-tert-butylphenol, 2,4-di-octylthiomethyl-6-methylphenol, 2,4-di-octylthiomethyl-6-ethylphenol or 2,6-di-dodecylthiomethyl-4-nonylphenol;
- 3) Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butyl-hydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate or bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate;
- 4) Tocopherols, for example α -, β -, γ - or δ -tocopherol or mixtures thereof (vitamin E);
- 5) Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol); 4,4'-thiobis(3,6-di-sec-amylphenol) or 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulphide;
- 6) Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis(4-methyl-6-(α -methylcyclohexyl)-phenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylenidenebis(4,6-di-tert-butylphenol), 2,2'-ethylenidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis(6-(α -methylbenzyl)-4-nonylphenol), 2,2'-methylene-bis(6-(α , α -dimethylbenzyl)-4-nonylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)-butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane,

ethylene glycol bis(3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate), bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclo-pentadiene, bis(2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl)terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane or 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)-pentane;

7) O-, N- and S-Benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl 4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulphide or isooctyl 3,5-di-tert-butyl-4-hydroxy-benzylmercaptoacetate;

8) Hydroxybenzylated malonates, for example-diocadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecyl mercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-malonate or di(4-(1,1,3,3-tetramethylbutyl)phenyl)2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate;

9) Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene or 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol;

10) Triazine compounds, for example 2,4-bis(octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine or 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)-isocyanurate;

11) Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzyl-phosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate or the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid;

12) Acylaminophenols, for example 4-hydroxyauranilide, 4-hydroxystearanilide or octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate;

- 13) Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid, β -(3,5-dicyclohexyl-4-hydroxyphenyl)-propionic acid, 3,5-di-tert-butyl-4-hydroxyphenylacetic acid or β -(5-tert-butyl-4-hydroxyphenyl)-3-thiabutyric acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethyl-hexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo(2.2.2)octane, glycerol or transesterification products based on natural triglycerides of, for example, coconut oil, rape seed oil, sunflower oil or colza oil;
- 14) Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine or N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine;

The previous list of items 1) through 14) contains examples of phenolic antioxidants which are well known in the prior art; and

- 15) Ascorbic acid (vitamin C);

- 16) Amine-type antioxidants, for example N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methyl-pentyl)-p-phenylenediamine, N,N'-bis(1-methyl-heptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di-(naphth-2-yl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulphonamido)diphenylamine, N, N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxy-diphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, e.g. p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylamino-phenol, 4-nonylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, di-(4-methoxyphenyl)-amine, 2,6-di-tert-butyl-4-dimethylamino-methyl-phenol, 2,4'-diamino-diphenylmethane, 4,4'-diamino-diphenylmethane, N,N,N',N'-tetramethyl-4,4'-diamino-diphenylmethane, 1,2-di-((2-methyl-phenyl)-amino)-ethane, 1,2-di-(phenylamino)propane, (o-tolyl)biguanide, di(4-(1',3'-dimethyl-butyl)-phenyl)amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a

mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/iso-hexyldiphenylamines, mixtures of mono- and dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octyl-phenothiazines, a mixture of mono- and dialkylated tert-octyl-phenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis-(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis-(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 2,2,6,6-tetramethylpiperidin-4-one or 2,2,6,6-tetramethylpiperidin-4-ol; and

17) Aliphatic or aromatic phosphites, esters of thiodipropionic acid or of thiodiacetic acid, or salts of dithiocarbamic or dithiophosphoric acid, 2,2,12,12-tetramethyl-5,9-dihydroxy-3,7,11-trithiatridecane or 2,2,15,15-tetramethyl-5,12-dihydroxy-3,7,10,14-tetrathiahexadecane.

Examples of metal passivators, for example for copper, are:

- 1) Benzotriazoles and their derivatives, for example 4- or 5-alkylbenzotriazoles (e.g. tolutriazole) and derivatives thereof, 4,5,6,7-tetrahydrobenzotriazole, 5,5'-methylenebisbenzotriazole; Mannich bases of benzotriazole or tolutriazole, such as 1-(di(2-ethylhexyl)aminomethyl)tolutriazole and 1-(di(2-ethylhexyl)aminomethyl)-benzotriazole; alkoxyalkylbenzotriazoles, such as 1-(nonyloxymethyl)-benzotriazole, 1-(1-butoxyethyl)-benzotriazole and 1-(1-cyclohexyloxybutyl)-tolutriazole;
- 2) 1,2,4-Triazoles and derivatives thereof, for example 3-alkyl(or aryl)-1,2,4-triazoles, Mannich bases of 1,2,4-triazoles, such as 1-(di(2-ethylhexyl)aminomethyl)-1,2,4-triazole; alkoxyalkyl-1,2,4-triazoles, such as 1-(1-butoxyethyl)-1,2,4-triazole; acylated 3-amino-1,2,4-triazoles;
- 3) Imidazole derivatives, for example 4,4'-methylenebis(2-undecyl-5-methyl-imidazole), bis((N-methyl)imidazol-2-yl)carbinol octyl ether;
- 4) Sulphur-containing heterocyclic compounds, for example 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2,5-dimercaptobenzothiadiazole and derivatives thereof; 3,5-bis(di(2-ethylhexyl)aminomethyl)-1,3,4-thiadiazolin-2-one; and
- 5) Amino compounds, for example salicylidenepropylenediamine, salicylaminoguanidine and salts thereof.

Examples of rust inhibitors are:

- 1) Organic acids, their esters, metal salts, amine salts and anhydrides, for example alkyl- and alkenylsuccinic acids and the partial esters thereof with alcohols, diols or hydroxy-carboxylic acids, partial amides of alkyl- and alkenylsuccinic acids, 4-nonylphenoxyacetic acid, alkoxy- and alkoxyethoxycarboxylic acids, such as dodecyloxyacetic acid, dodecyloxy(ethoxy)acetic acid and the amine salts thereof, and also N-oleoylsarcosine, sorbitan monooleate, lead naphthenate, alkenylsuccinic anhydrides, for example dodecenylsuccinic anhydride, 2-(2-carboxyethyl)-1-dodecyl-3-methylglycerol and its salts, especially sodium and triethanolamine salts;
- 2) Nitrogen-containing compounds, for example:
 - i) Primary, secondary or tertiary aliphatic or cycloaliphatic amines and amine salts of organic and inorganic acids, for example oil-soluble alkylammonium carboxylates, and also 1-(N,N-bis(2-hydroxyethyl)amino)-3-(4-nonylphenoxy)propan-2-ol;
 - ii) Heterocyclic compounds, for example: substituted imidazolines and oxazolines, 2-heptadecenyl-1-(2-hydroxyethyl)-imidazoline;
- 3) Phosphorus-containing compounds, for example Amine salts of phosphoric acid partial esters or phosphonic acid partial esters, zinc dialkyldithiophosphates;
- 4) Sulphur-containing compounds, for example: barium dinonylnaphthalene-sulphonates, calcium petroleumsulphonates, alkylthio-substituted aliphatic carboxylic acids, esters of aliphatic 2-sulphocarboxylic acids and salts thereof; and
- 5) Glycerol derivatives, for example: glycerol monooleate, 1-(alkylphenoxy)-3-(2-hydroxyethyl)glycerols, 1-(alkylphenoxy)-3-(2,3-dihydroxypropyl)glycerols, 2-carboxyalkyl-1,3-dialkylglycerols.

Useful viscosity index improvers include any of the polymers which impart enhanced viscosity properties to the finished oil. They are generally hydrocarbon-based polymers having a molecular weight, Mw, in the range of between about 2 000 to 1 000 000, preferably about 50 000 to 200 000. Viscosity index improver polymers include olefin copolymers, for example, ethylene-propylene copolymers, ethylene-(iso)-butylene copolymers, propylene-(iso)-butylene copolymers, ethylene-polyalphaolefin copolymers, polymethacrylates; styrene-diene block copolymers, for example, styrene-isoprene copolymers, and star copolymers; polyacrylates, vinylpyrrolidone/methacrylate copolymers, polyvinylpyrrolidones, polybutenes, sty-

rene/acrylate copolymers, and polyethers. Viscosity index improvers may be monofunctional or multifunctional, such as those bearing substituents that provide a secondary lubricant performance feature, such as dispersancy, pour point depression, etc.

5 Examples of pour point depressants are: Polymethacrylates or alkylated naphthalene derivatives;

Examples of dispersants/surfactants are: Polybutenylsuccinamides or -imides, polybutenylphosphonic acid derivatives, and basic magnesium, calcium and barium sulphonates, phenolates and salicylates;

Examples of antifoams are: Silicone oils and polymethacrylen;

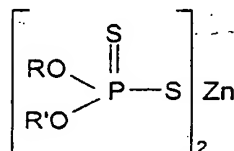
10 The demulsifiers are, for example, selected from polyetherpolyols and dinonylnaphthalene-sulphonates;

The friction modifiers are, for example, selected from: fatty acids and their derivatives (i.e. natural esters of fatty acids, such as glycerol monooleate), amides, imides and amines (i.e. oleylamine), sulphur containing organo molybdenum dithiocarbamates, sulphur-phosphorus
15 containing organo molybdenum dithiophosphates, sulphur-nitrogen containing organo molybdenum compounds based on dispersants, molybdenum carboxylate salts, molybdenum-amine complexes, molybdenum amine/alcohol/amid complexes and molybdenum cluster compounds, Teflon™ and molybdenum disulphide;

Examples of antiwear additives are:

20 Sulphur- and/or phosphorus- and/or halogen-containing compounds, such as sulphurised olefins and vegetable oils, zinc dialkyldithiophosphates, tritolyl phosphate, tricresyl phosphate, chlorinated paraffins, alkyl and aryl di- and trisulphides, amine salts of mono- and dialkyl phosphates, amine salts of methylphosphonic acid, diethanolaminomethyltolyl triazole, di-(2-ethylhexyl)-aminomethyltolyl triazole, derivatives of 2,5-dimercapto-1,3,4-thiadiazole, ethyl(bisisopropoxyphosphinothioyl)thiopropionate, triphenyl thiophosphate (triphenyl
25 phosphorothioate), tris(alkylphenyl) phosphorothioates and mixtures thereof, for example tris(isononylphenyl) phosphorothioate, diphenylmonononylphenyl phosphorothioate, isobutylphenyl diphenyl phosphorothioate, the dodecylamine salt of 3-hydroxy-1,3-thiaphosphetan 3-oxide, trithiophosphoric acid 5,5,5-tris-isooctyl 2-acetate, derivatives of 2-mercaptobenzothiazole, such as 1-N,N-bis(2-ethylhexyl)aminomethyl-2-mercapto-1H-1,3-benzothiazole,
30 and ethoxycarbonyl 5-octyldithiocarbamate;

Dihydrocarbyl dithiophosphate metal salts where the metal is aluminum, lead, tin manganese, cobalt, nickel, zinc or copper, but most often zinc. The zinc salt (zinc dialkyl dithiophosphate) is represented as



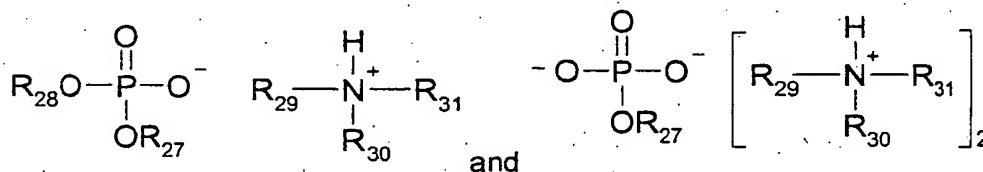
- 5 where R and R' are independently of one another C₁-C₂₀alkyl, C₃-C₂₀alkenyl, C₅-C₁₂cycloalkyl, C₇-C₁₃aralkyl or C₆-C₁₀aryl, for example R and R' are independently C₁-C₁₂alkyl;

Suitable antiwear additives are described in *U.S. Patent Specification* Nos. 4,584,021;

5,798,321; 5,750,478; 5,801,130; 4,191,666; 4,720,288; 4,025,288; 4,025,583 and WO

095/20592, amines for example polyalkylene amines, such as ethylene diamine, diethylene

- 10 triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, nonaethylene decylamine and aryl amines as described in *United States Patent Specification* No. 4,267,063, salts of amine phosphates comprising specialty amines and mixed mono- and di-acid phosphates; the mono- and di-acid phosphate amines have the structural formulae:



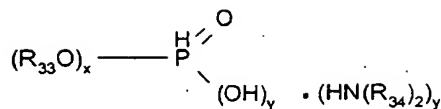
- 15 Wherein R₂₇ is hydrogen, C₁-C₂₅ linear or branched chain alkyl, which is unsubstituted or substituted by at least one C₁-C₆alkoxy groups, a saturated acyclic or alicyclic group, or aryl
R₂₈ is C₁-C₂₅ linear or branched chain alkyl, which is unsubstituted or substituted by at least one C₁-C₆alkoxy groups, a saturated acyclic or alicyclic group, or aryl;

- R₂₉ is hydrogen, C₁-C₂₅ linear or branched chain alkyl, a saturated or unsaturated acyclic or
20 alicyclic group, or aryl; and are hydrogen or C₁-C₁₂ linear or branched chain alkyl; and

R₃₀ and R₃₁ are, each independently of the other, C₁-C₂₅ linear or branched chain alkyl, a saturated or unsaturated acyclic or alicyclic group, or aryl. Preferably, R₂₇ and R₂₈ are linear or branched C₁-C₁₂ alkyl; and R₂₉, R₃₀ and R₃₁ are linear or branched C₁-C₁₈ alkyl;

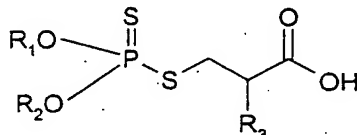
- 25 Irgalube® 349 (Ciba Specialty Chemicals) has been found to be very useful, particularly by enhancing the wear performance of the base oil such that it meets stringent military performance specifications; IRGALUBE 349 corresponds to the formula

- 16 -



Wherein R_{33} is n-hexyl, R_{34} is C_{11} - C_{14} branched alkyl, and when $x=1$ then $y=2$; when $x=2$ then $y=1$.

Other conventional antiwear additives are compounds of the formula



5

in which R_1 and R_2 independently of one another are C_3 - C_{18} alkyl, C_5 - C_{12} cycloalkyl, C_5 - C_6 cycloalkylmethyl, C_9 - C_{10} bicycloalkylmethyl, C_9 - C_{10} tricycloalkylmethyl, phenyl or C_7 - C_{24} alkylphenyl or together are $(\text{CH}_3)_2\text{C}(\text{CH}_2)_2$ and R_3 is hydrogen or methyl.

10 A representative compound is Irgalube® 353 (Ciba Specialty Chemicals), a dialkyl dithiophosphate ester, CAS Reg. No. 268567-32-4.

The lubricating oil compositions can contain, in addition to the antioxidant additives, other known additives. These include antiknocking agents, such as tetraalkyl lead compounds, lead scavengers, such as haloalkanes (e.g., ethylene dichloride and ethylene dibromide), deposit preventers or modifiers, such as triaryl phosphates, dyes, cetane improvers, antioxidants, 15 such as 2,6-di-tert-butyl-4-methylphenol, rust inhibitors, such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, upper cylinder lubricants and anti-icing agents.

The present antioxidant compositions can be introduced into the lubricating oil in manners known per se. The compounds are readily soluble in oils. They may be added directly to the 20 lubricating oil or they can be diluted with a substantially inert, normally liquid organic diluent, such as naphtha, benzene, toluene, xylene or a normally liquid oil or fuel to form an additive concentrate or master batch. These concentrates generally contain from about 10% to about 90% by weight additive and may contain at least one other additional additives. The present antioxidant compositions may be introduced as part of an additive package.

25 The present invention is further illustrated by the following Examples:

Example 1: Octyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate

Examples 2-13: Antioxidant Compositions

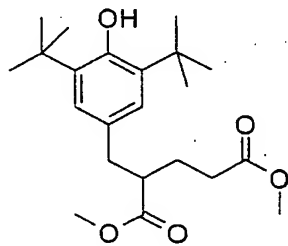
Examples 14-18: Application Examples

Example 1: Octyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (256.0 g, 0.88 mol) and isooctanol (133.0 g, 0.91 mol) are added to a laboratory reactor equipped with the necessary auxiliary equipment. The mixture is heated to 85°C under a reduced pressure of 0.04 bar. After fifteen minutes, the reduced pressure is released and aluminum isopropoxide (1.77 g, 0.0087 mol, Rhone-Poulenc, Manalox® 130) is added. The reaction mass is heated to 130°C, while under a reduced pressure of 0.1 bar. After two hours, the reaction mass is heated to 165°C while under a reduced pressure of 0.04 bar for one hour. The excess isooctanol is removed by reduced pressure distillation at 165°C. The title compound (331.0 g, 97% yield) is obtained as a light yellow oil whose assay is 97% as judged by calibrated gas chromatography.

Example 2: Antioxidant Compositions

Phenolic antioxidants and phosphites are crystallized from organic solvents; for example, methanol and isopropanol. These solvent streams are blended together and the solvents are recovered by distillation. The residue that remains after solvent distillation contains (as analysed by calibrated gas chromatography): 2,6-di-tert-butylphenol: 5.4 wt%; 2,4-di-tert-butylphenol: 0.35 wt%; methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate: 21.2 wt%; Compound A: 29.0 wt%; thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate): 3.7 wt%; neopentane tetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate): 2.2 wt%; pentaerythritol tris(3,5-di-tert-butyl-4-hydroxyhydrocinnamate): 5.9%; pentaerythritol di(3,5-di-tert-butyl-4-hydroxyhydrocinnamate): 4.3 wt%; n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate: 4.2 wt%; and, tris(2,4-di-tert-butylphenyl) phosphite: 0.3 wt%.



Compound A is
zyl)glutarate.

: Dimethyl α -(3,5-di-tert-butyl-4-hydroxyben-

Example 3: Antioxidant Compositions

Phenolic antioxidants are purified by distillation during their manufacture. The distillation residue that remains contains (as analysed by calibrated gas chromatography): 2,6-di-tert-

butylphenol: 42.3 wt%; 2,4-di-tert-butylphenol: 0.85 wt%; methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate: 29.0 wt%; and, Compound A (structural formula in Ex. 2): 27.9 wt%.

Example 4: Antioxidant Compositions

5 The composition as obtained according to Example 1 (80.0 g, 0.21 mol), Example 2 (20.0 g), and methanol (2.8 g, 0.088 mol) are added to a flask and stirred until homogeneity. The solution is then heated under reduced pressure to remove any moisture and methanol. Distillation is continued until a constant weight is received. The antioxidant composition is received (99.0 g) as a light amber oil.

Example 5: Antioxidant Compositions

10 The compositions according to Examples 1 (90.0 g, 0.23 mol), Example 2 (10.0 g), and methanol (1.4 g, 0.044 mol) are added to a flask and stirred until homogeneity. The solution is then heated under reduced pressure to remove any moisture and methanol. Distillation is continued until a constant weight is received. The antioxidant composition is received (98.0 g) as a light amber oil.

Example 6: Antioxidant Compositions

15 The compositions according to Example 1 (95.0 g, 0.24 mol), Example 2 (5.0 g), and methanol (0.7 g, 0.022 mol) are added to a flask and stirred until homogeneity. The solution is heated under reduced pressure to remove any moisture and methanol. Distillation is continued until a constant weight is received. The antioxidant composition is received (99.0 g) as a light
20 amber oil.

Example 7: Antioxidant Compositions

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (254.0 g, 0.87 mol), isooctanol (142.5 g, 1.09 mol, Exxon 8 from Exxon), and the composition according to Example 2 (51.0 g) are added to a reaction flask and heated to 85°C under reduced pressure. The reduced pressure
25 is released and aluminum isopropoxide (5.0 g, 0.025 mol, Rhone Poulenc, MANALOX 130) is added portion wise. Reduced pressure is applied while heating to 130°C. After seven hours, the temperature is increased to 165°C for three hours. The excess isooctanol is removed by distillation under reduced pressure. The antioxidant composition is received (380.2 g) as a light amber oil and contains 87.6 wt% of isooctyl esters (as a mixture) by cali-
30 brated gas chromatography.

Example 8: Antioxidant Compositions

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (125.0 g, 0.43 mol), isooctanol (75.0 g, 0.58 mol, Exxal 8 from Exxon), and the composition according to Example 3 (30.3 g) are added to a reaction flask and heated to 87°C under reduced pressure. The reduced pressure is released and aluminum isopropoxide (0.78 g, 0.004 mol, Rhone Poulenc, MANALOX 130) is added. A reduced pressure of 0.13 bar is applied while heating to 150°C. After two and one-half hours, the excess isooctanol is removed by distillation under reduced pressure. The antioxidant composition is received (187.3 g) as a light amber oil and contains 88.2 wt% of isooctyl esters (as a mixture) by calibrated gas chromatography.

10 Example 9: Antioxidant Compositions

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (10.224 g, 34.97 mol), isooctanol (6002.0 g, 46.1 mol, Exxal 8 from Exxon), and the composition according to Example 3 (1139.0 g) are added to a reaction flask and heated to 100°C under reduced pressure. The reduced pressure is released and aluminum isopropoxide (244.2 g, 1.25 mol, Rhone Poulenc, MANALOX 130) is added. A reduced pressure is applied while heating to 150°C. After one hour, the temperature is increased to 165°C for three hours. The excess isooctanol is removed by distillation under reduced pressure. The antioxidant composition is received (15.164 g) as a light amber oil and contains 90.8 wt% of isooctyl esters (as a mixture) by calibrated gas chromatography.

20 Example 10: Antioxidant Compositions

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (8640 g, 29.5 mol), isooctanol (5339.0 g, 41 mol, Exxal 8 from Exxon), and the composition according to Example 2 (2229.0 g) are added to a reaction flask and heated to 100°C under reduced pressure. The reduced pressure is released and aluminum isopropoxide (120.0 g, 0.62 mol, Rhone Poulenc, MANALOX 130) is added. A reduced pressure is applied while heating to 150°C. After two and one-half hours, the excess isooctanol is removed by distillation under reduced pressure. The antioxidant composition is received (13,497 g) as a light amber oil and contains 88.1 wt% of isooctyl esters (as a mixture) by calibrated gas chromatography.

Example 11: Antioxidant Compositions

30 Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (8909.0 g, 30.5 mol), isooctanol (4999.0 g, 38.4 mol, Exxal 8 from Exxon), and the composition according to Example 2 (1815.0 g) are added to a reaction flask and heated to 100°C under reduced pressure. The reduced pres-

sure is released and aluminum isopropoxide (174.0 g, 0.89 mol, Rhone Poulenc, MANALOX 130) is added portion wise. A reduced pressure is applied while heating to 130°C. After seven hours, the temperature is increased to 165°C for three hours. The excess isooctanol is removed by distillation under reduced pressure. The antioxidant composition is received (13,834 g) as a light amber oil and contains 89.0 wt% of isooctyl esters (as a mixture) by calibrated gas chromatography.

Example 12: Antioxidant Compositions

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate (100 kg), isooctanol (62.9 kg Exxal 8 from Exxon), and the composition according to Example 3 (30.7 kg) are added to a reactor and heated to 100°C under reduced pressure. The reduced pressure is released and aluminum isopropoxide (650.0 g, 3.3 mol, Rhone Poulenc, MANALOX 130) is added. A reduced pressure of 0.2 bar is applied while heating to 150°C. After two and one-half hours, the excess isooctanol is removed by distillation under reduced pressure. The antioxidant composition is received (356.9 lbs.) as a light amber oil and contains 85.9 wt% of isooctyl esters (as a mixture) by calibrated gas chromatography.

Example 13: Antioxidant Compositions

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, isooctanol, and the composition according to Example 3 are added to a reactor and heated to 100°C under reduced pressure. The reduced pressure is released and MANALOX 130 is added. A reduced pressure of 0.2 bar is applied while heating to 150°C. After two and one-half hours, the excess isooctanol is removed by distillation under reduced pressure. Under these reaction conditions, dimethyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate, diisooctyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate, and monomethyl-monoisooctyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate are produced.

Example 14: Flash Point Test

A flash point test is performed on the examples to ensure no volatile, flammable components are present. The samples are tested using an Erdco Rapid Tester Model RT-1 at 22.2°C, 60.6 C, and 92.8°C. The results are summarized below:

Example	Flash Point [°C]
4	>199
5	>199
6	>199
8	>199

The results indicate that the compositions do not contain volatile, flammable components.

Example 15: TGA Analysis

- 5 A thermogravimetric analysis (TGA) is performed with the composition according to some representative Examples to evaluate their volatility at elevated temperatures. The weight loss of samples as temperature is increased is monitored and the temperatures at which a 10% and 50% weight loss occur are noted. The results are summarized below:

Example	Temperature 1 [at 10% loss]	Temperature 2 [at 50% loss]
1	216	260
9	224	271
11	228	275
10	230	276

The data show that the compositions are less volatile than the compound according to Example 1, a compound known in the prior art.

10 Example 16: High Temperature Deposit Test

- The compositions are evaluated for their ability to reduce deposit formation in lubricants, such as passenger car motor oil and diesel engine oil formulations. Thin films of oil on steel cups are heated at 230°C in the Alcor Micro Carbon Residue Tester for increasing periods of time. After each time interval the cups are washed with hexane and the amount of residue
- 15 left behind is determined. The difference in percent deposits formed by a base formulation for a set time interval is compared with those formed by the base formulation plus stabilizers. The magnitude of a beneficial decrease in deposit formation is rated as a ratio that is designated the performance index (PI). The higher the PI, the better the sample is at controlling deposit formation. Each formulation contains 1.5% by weight of stabilizer in a fully

formulated SAE 5W-30 passenger car motor oil, GF-4 type formulation with 0.05 % phosphorus by weight.

Example	Performance Index [PI]
1	6
11	24
10	34
12	45
9	67

Example 17: Hot Tube Test

- 5 The compositions are evaluated in a test that measures the deposit forming tendencies of an oil sample. In the test, oil droplets are pushed upward by compressed air inside a glass capillary tube that is heated to 248°C. Test oil percolates upward through the tube for 16 hours forming a lacquer on the inner wall of the tube. At the conclusion of the test, the tube is washed, dried and rated for cleanliness on a 0-10 scale (0: dirty, 10: clean).
- 10 Each formulation contains 1.5% by weight of stabilizer in a fully formulated SAE 5W-30 passenger car motor oil, GF-4 type formulation with 0.05 % phosphorus by weight. The data are summarized below and represent the average of two tests.

Example	Cleanliness
1	4.5
9	4.7
10	4.8
11	5.0

Example 18: HPDSC Test

- 15 High pressure differential scanning calorimetry (HPDSC) is an analytical technique that evaluates oxidative performance of additives in various substrates. A TA Instruments Model 2920 is used for the evaluations. The test is run under pressure to prevent volatilization of the material to be evaluated. In this evaluation, the samples, in aluminum pans, are heated

isothermally at 210°C in a cell pressurized to 0.519 bar with air. The time until an exothermic reaction occurs (oxidation induction time) is measured. The longer the oxidation induction period, the more stable the sample.

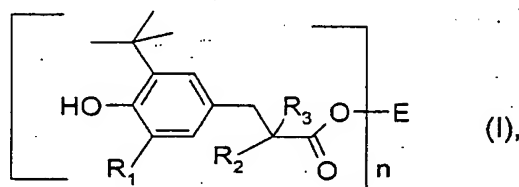
Each formulation contains 1.5% by weight of stabilizer in a fully formulated SAE 5W-30 passenger car motor oil, GF-4 type formulation with 0.05 % phosphorus by weight. The data are summarized below and represent the average of two tests.

Example	Oxidation Induction Time [minutes]
1	94
9	95
11	95
12	105

Claims

1. A lubricating oil composition comprising

a) At least one hindered phenolic antioxidant compound of formula (I),



5 Wherein

 R_1 is alkyl of 1 to 4 carbon atoms; n is an integer from 1 to 4; R_2 is H or has the meanings of R_3 ; R_3 is $-(CH_2)_x-COOR_4$, where x is 1 to 10;10 R_4 is straight or branched chain alkyl of 1 to 24 carbon atoms or the group of the partial formula E;When n is 1, E is straight or branched chain alkyl of 1 to 24 carbon atoms;When n is 2, E is straight or branched chain alkylene of 2 to 12 carbon atoms or said alkylene interrupted by one to five O or S atoms;15 When n is 3, E is a straight or branched chain alkanetriyl of 3 to 6 carbon atoms; andWhen n is 4, E is pentaerythrityl;

b) At least one additional antioxidant compound; and

c) A base fluid.

20 2. A composition according to claim, wherein the component a) includes hindered phenolic antioxidant compounds of the formula (I) selected from the group consisting of:

Dimethyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate,Diisooctyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate, andMonomethyl-monoisooctyl α -(3,5-di-tert-butyl-4-hydroxybenzyl)glutarate.

25 3. A composition according to claim 1, wherein the phenolic antioxidant compounds of component b) are selected from the group consisting of:

- n-Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Isooctyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
1,3,5-tris(3,5-Di-tert-butyl-4-hydroxybenzyl)isocyanurate,
5 Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
1,3,5-Trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene,
3,6-Dioxaoctamethylene bis(3-methyl-5-tert-butyl-4-hydroxyhydrocinnamate),
2,6-Di-tert-butyl-p-cresol,
2,2'-Ethylidene-bis(4,6-di-tert-butylphenol),
10 1,3,5-tris(2,6-Dimethyl-4-tert-butyl-3-hydroxybenzyl)isocyanurate,
1,1,3-tris(2-Methyl-4-hydroxy-5-tert-butylphenyl)butane,
1,3,5-tris[2-(3,5-Di-tert-butyl-4-hydroxyhydrocinnamoyloxy)ethyl] isocyanurate,
3,5-Di-(3,5-di-tert-butyl-4-hydroxybenzyl)mesitol,
Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
15 1-(3,5-Di-tert-butyl-4-hydroxyanilino)-3,5-di(octylthio)-s-triazine,
N,N'-Hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide),
Calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate),
Ethylene bis[3,3-di(3-tert-butyl-4-hydroxyphenyl)butyrate],
Octyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate,
20 bis(3,5-Di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide,
N,N'-bis[2-(3,5-Di-tert-butyl-4-hydroxyhydrocinnamoyloxy)-ethyl]oxamide,
2,6-Di-tert-butylphenol,
2,4-Di-tert-butylphenol,
Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
25 Pentaerythritol tris(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
Pentaerythritol di(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
tris(2,4-Di-tert-butylphenyl) phosphite,

Di-n-octadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate,
N,N-Di-(C₁₄-C₂₄alkyl)-N-methylamine oxide,
N,N-Dialkylhydroxylamine, and
N,N-Di(hydrogenated tallow)hydroxylamine.

- 5 4. A composition according to claim 1, wherein the phenolic antioxidant compounds of component b) are selected from the group consisting of:

n-Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Isooctyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
10 Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
2,2'-Ethylidene-bis(4,6-di-tert-butylphenol),
1,1,3-tris(2-Methyl-4-hydroxy-5-tert-butylphenyl)butane,
Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
N,N'-Hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide),
15 Ethylene bis[3,3-di(3-tert-butyl-4-hydroxyphenyl)butyrate],
bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide,
2,6-Di-tert-butylphenol,
2,4-Di-tert-butylphenol,
Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
20 Pentaerythritol tris(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),
Pentaerythritol di(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), and
tris(2,4-Di-tert-butylphenyl) phosphite.

5. A composition according to claim 1, wherein the phenolic antioxidant compounds of component b) are selected from the group consisting of:

25 n-Octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Isooctyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,
Neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

2,6-Di-tert-butylphenol,

2,4-Di-tert-butylphenol,

Methyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate,

5 Pentaerythritol tris(3,5-di-tert-butyl-4-hydroxyhydrocinnamate),

Pentaerythritol di(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), and

tris(2,4-Di-tert-butylphenyl) phosphite.

6. A composition according to claim 5, which additionally comprises

10 d) At least one compound selected from the group consisting of other antioxidants, metal passivators, rust inhibitors, corrosion inhibitors, viscosity index improvers, extreme pressure agents, pour point depressants, solid lubricants, dispersants, detergents, antifoams, colour stabilizers, further extreme pressure additives, demulsifiers, friction modifiers, and antiwear additives.

7. A method of improving oxidative performance in a lubricating oil composition comprising

15 b) At least one antioxidant compound according to component b), as defined above; and

c) A base fluid,

which method comprises incorporating into said lubricating oil composition at least one compound of component a) formula (I) as defined in claim 1.

8. An antioxidant composition, which comprises a mixture of

20 a) At least one hindered phenolic antioxidant compound of formula (I), wherein R₁, R₂, R₃, R₄ and E are as defined in claim 1; and

b) At least one additional antioxidant compound.

9. An antioxidant composition according to claim 8, which additionally comprises

25 e) At least one organic material subject to the deleterious effects of oxidative, thermal, or light-induced degradation.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/053883

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10M129/00 C10M129/72 C10M135/26 C10M141/06 C10M141/10
C10M141/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 659 863 A (BURTON ET AL) 21 April 1987 (1987-04-21) column 1, line 1 - line 30 column 7, line 21 - column 8, line 42 figures; examples	1-9
A	US 5 478 875 A (DUBS ET AL) 26 December 1995 (1995-12-26) column 1, line 1 - line 40 column 24, line 1 - column 25, line 25 column 29, line 17 - column 31, line 25 column 34, line 20 - column 37, line 23	1-9
A	US 3 637 585 A (PATRICK D. BEIRNE) 25 January 1972 (1972-01-25) the whole document	1-9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

28 September 2005

Date of mailing of the international search report

18/11/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Dötterl, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/053883

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4659863	A	21-04-1987	NONE	
US 5478875	A	26-12-1995	BR 9301482 A	13-10-1993
			CA 2093488 A1	09-10-1993
			DE 59306149 D1	22-05-1997
			DK 565487 T3	20-05-1997
			EP 0565487 A2	13-10-1993
			ES 2101994 T3	16-07-1997
			HK 1005024 A1	18-12-1998
			JP 3668898 B2	06-07-2005
			JP 6025085 A	01-02-1994
US 3637585	A	25-01-1972	NONE	